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## (54) PREVENTION OF SILICA PORE OBSTRUCTION IN CRYSTALLINE ALUMINOSILICATES

- (71) We, MOBIL OIL CORPORATION, a corporation organised under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- Crystalline aluminosilicates are synthesized, generally speaking, from a reaction mixture comprising mixtures of oxides including sodium oxide, alumina, silica and water. Generally speaking, they are crystallized under alkaline conditions. After a gel is formed, the gel is allowed to remain in the presence of the mother liquor until the material crystallizes. It is subsequently removed, washed until the pH of the filtrate becomes constant and dried.
- It has been found that some preparations of crystalline aluminosilicates, especially those with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios above 6, contain a substantial amount of occluded silica which impairs subsequent base exchange into a more catalytically-active form as well as ultimate catalytic activity and adsorption capacity. Soluble silicates which may become entrained within the pores of the zeolites present special problems. If the zeolite is subsequently contacted with a rare earth chloride solution to prepare a rare earth exchanged form, the occluded silicates will be converted into a rare earth silicate which, in subsequent use in catalytic cracking, has a high tendency to form coke and thus decrease the overall selectivity of the cracking catalyst. Generally speaking, the occluded silica prevents or impairs the full ion exchange of the material because it blocks certain exchange sites from the incoming exchanging cations. It has thus become desirable to provide a means whereby these crystalline aluminosilicate zeolites can be rendered free of occluded silica.
- Broadly, this invention contemplates a method for decreasing silica occlusion in crystalline aluminosilicate zeolites, possessing  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  ratios greater than 6.
- According to the invention we provide a method of synthesizing a crystalline aluminosilicate zeolite having a silica: alumina mole ratio greater than 6, which method comprises forming a reaction mixture containing silica, alumina, cations and water in the proportions required for crystallization therefrom of a crystalline aluminosilicate zeolite of a predetermined composition, said reaction mixture further containing an amount surplus to said required proportions and having no influence upon said predetermined composition, of a solution of an alkali metal salt (as herein defined), and recovering from said mixture a crystalline aluminosilicate zeolite substantially free of pore obstruction by silica and having said predetermined composition. The normality of the salt solution is preferably less than 1.
- The alkali metal salts used according to the invention must not change the concentration in the reaction mixture of the primary framework reagents, namely silica and alumina; accordingly, silicates and aluminates are excluded from their scope. On the other hand, ammonium salts (subject to the abovementioned exclusion) function as well as actual alkali metal salts in the method of the invention and therefore are included within the scope of the term.
- The present invention offers a means of improving the activity and selectivity of catalytic forms of the crystalline aluminosilicate by the removal of occluded silica. Occluded silica impairs catalytic activity and selectivity by making catalytic sites unavailable to the reactants, by increasing the resistance to mass transfer of reactants and products in and out of the crystalline aluminosilicate and by increasing the tendency

of forming undesirable products on or within the crystalline aluminosilicate during subsequent ion exchange procedures.

It has been discovered that the techniques of this invention for eliminating occluded silica are most effective, from the catalytic point of view, when the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of the crystalline aluminosilicate is greater than 6. Crystalline aluminosilicates with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios above 6, such as ZSM-4 and ZSM-5, shown a large appreciation in catalytic activity when comparing identical preparations with and without salt addition. Similar experiments with faujasites showed no appreciation with added salt in the reaction mix in terms of catalytic activity.

Similarly, the dynamic as well as the equilibrium adsorption properties will be enhanced by the elimination of occluded  $\text{SiO}_2$  which makes unavailable surface area or adsorption sites in the crystalline aluminosilicate and obstructs the pore openings so that the rate of adsorbate is adsorbed within the crystalline aluminosilicate is reduced.

A preferred method of carrying out the present invention resides in introducing the salt into the reaction mixture prior to gel formation via one of the forming solutions. The presence of the salt acts to prevent the occlusion of silica within the eventual crystal structure of the zeolite material. In another embodiment, of a particularly desirable type, the salt is introduced into the crystallization forming mixture, i.e. into the mother liquor in the presence of the cogelled silica alumina mixture, which, upon time and temperature, will crystallize into the desired crystalline aluminosilicate zeolite.

The technique of the present invention is very effective in increasing the rate of filtration of zeolite slurries as well as the ease by which soluble impurities are removed by washing. When salt is added to a sodium ZSM-4 reaction mixture, the filtration rate is observed to be more than double with definite improvements in the handling properties of the filter cake. These improvements in the handling properties of the material are especially important in ion exchanging large batches of the material as in plant operations.

It is contemplated in this invention that the alkali metal and ammonium salts which may be added to the crystalline aluminosilicate synthesis reaction mixture to reduce silica occlusion also include mixtures of alkali metal and ammonium salts provided the composition of the mixture does not disrupt the cation balance in the crystallized product, change the species of the crystallized product from that desired or prevent crystallization of a crystalline aluminosilicate.

Zeolites which can be prepared in accordance with the methods of the present invention are the synthetic zeolites. These includes zeolites L, T, alpha, beta, mordenite, synthetic offretite, synthetic erionite, ZSM-4, ZSM-5 and other synthetic zeolites with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios greater than 6. These zeolites having an average pore size of between about 5 and 15 Angstroms benefit particularly by the present invention since the effect of occluded silica on these zeolites can be to render the substance appreciably non-porous. Once the porosity is improved by the removal of the occluded silica, the zeolites can be converted with a form where they can be suitable for catalysis.

In order to more fully illustrate the nature of the present invention and the manner of practicing the same, the following Examples are presented:

#### EXAMPLE 1

In order to illustrate the enhancement in catalytic activity brought about by the reduction of silica occlusion, four ZSM-4 samples were synthesized differing only in the amount of sodium chloride added to the reaction mixture.

The basic method of formulation was that 130 grams of Georgia Kaolin, calcined 6 hours at  $1700^\circ\text{F}$ ., was added to a solution containing 361 grams of Q-brand sodium silicate, 60 grams of NaOH (98.2 percent NaOH) and 69 grams of a 50 percent weight percent water solution of tetramethylammonium chloride. In the preparations using added sodium chloride, the salt was added to the solution prior to the clay addition. After thorough mixing on a Waring Blender, the mixture was transferred to a polypropylene jar and placed into a steam chest at  $100^\circ\text{C}$ . to crystallize. After crystallization to ZSM-4 was apparently complete, the material was removed from the steam chest, washed free of excess alkali and unreacted soluble silicates, and dried at  $120^\circ\text{C}$ . The dried samples were then given six 1 hour ion exchanges at  $180$ — $200^\circ\text{F}$ . using 500 grams of 10 weight percent  $\text{NH}_4\text{Cl}$  solution per 50 grams of solid sample. The samples were then washed chloride free, dried at  $120^\circ\text{C}$ ., and calcined for 1 hour at  $1000^\circ\text{F}$ . in 5 percent oxygen atmosphere saturated with water vapor.

Four samples were prepared in this manner with 0, 20, 40 and 60 grams, respectively, of sodium chloride incorporated into the reaction mixture. The catalysts so prepared were evaluated for catalytic activity using the low temperature toluene disproportionation test, LTD, described below. The catalytic activities shown in the follow-

ing table clearly indicate the enhancement in catalytic activity brought about by the reduction of silica occlusion by adding salt to the zeolite synthesis reaction mixture.

Effect of "Salting" on HZSM-4 Catalytic Activity					
5	NaCl in reaction mixture, g.	0	20	40	60
	LTD Activity $k_1$ , l/mole-sec. $\times 10^6$	2.4	60	49	82
					5

#### EXAMPLE 2

To further illustrate the enhancement of the catalytic activity brought about by the reduction of silica occlusion, three ZSM-4 samples were synthesized differing in that one sample had no salt added to the gel mixture and the other two samples had  $\text{Na}_2\text{SO}_4$  added to the gel mixture, differing only in the amount of  $\text{Na}_2\text{SO}_4$  added. The general formulation and preparative procedure is as follows: A silicate solution was prepared from 1,930 grams of Q-brand sodium silicate, 374 grams of 50 weight percent aqueous NaOH solution, 103 grams of 50 weight percent aqueous tetramethylammonium chloride solution and 952 grams of water. To this solution was added a solution, containing 326 grams of  $\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}$  and 575 grams of water, with agitation. At this stage, the  $\text{Na}_2\text{SO}_4$  was added to two of the three preparations. The gel mixtures were then transferred to polypropylene containers and transferred to a steam chest to crystallize at 180–200°F. When crystallization to ZSM-4 was apparently complete, the samples were removed from the steam chest, washed free of excess alkali and soluble silicates. The samples were then given six 1 hour ion exchanges at 180–200°F. using 500 grams of 5 weight percent  $\text{NH}_4\text{Cl}$  solution per 50 grams of dried sample. The samples were then washed chloride free, dried at 120°C. and calcined 1 hour at 1000°F. in a 5 percent oxygen atmosphere saturated with water vapor.

These three samples of ZSM-4 were prepared with 0, 200 and 300 grams of  $\text{Na}_2\text{SO}_4$  added to the gel mixture prior to crystallization. The catalysts so prepared were evaluated for catalytic activity using the low temperature toluene disproportionation test, LTD. The catalytic activities shown in the following table clearly demonstrate the improved activity obtained by reducing the silica occlusion.

Effect of "Salting" on HZSM-4 Catalytic Activity					
30	$\text{Na}_2\text{SO}_4$ in reaction mixture, g.	0	200	300	
	LTD, Activity $k_1$ , l/mole-sec. $\times 10^6$	30.2	50.6	50.4	30

#### EXAMPLE 3

To still further illustrate the improvement in catalytic activity resulting from a reduction in silica occlusion of crystalline aluminosilicates, two samples of ZSM-5, a highly siliceous crystalline aluminosilicate having  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio > 50, were prepared. ZSM-5 is described in Belgium Patent 713,576 of October 11, 1968. One sample contained added NaCl in the zeolite synthesis reaction mixture while the other preparation did not in all other respects, the preparations were identical.

The formulation and preparation of these samples were as follows: A silicate solution was prepared containing 44.7 pounds of Q-brand sodium silicate, 5.6 pounds of tetrapropyl ammonium bromide and 84 pounds of water. To this was added a sodium aluminate solution containing 0.56 pounds of sodium aluminate (41.8 percent  $\text{Al}_2\text{O}_3$ , 33.5 percent  $\text{Na}_2\text{O}$ ) and 14 pounds of  $\text{H}_2\text{O}$ . To this mixture was added a sulfuric acid solution containing 4.47 pounds of  $\text{H}_2\text{SO}_4$  (97 percent) and 14.0 pounds of water. For the sample containing added salt, a solution of 16.7 pounds of NaCl and 20 pounds of water was added at this point in the preparation. After thorough mixing, the mixture was heated to 200–212°F. and held at this temperature until crystallization to ZSM-5 was apparently complete. The samples of the crystalline aluminosilicate were then separated from the mother liquor and washed free of excess alkali and soluble silicates. The crystalline aluminosilicates were then dried and calcined 10 hours at 1000°F. in air. After calcination, the zeolite samples were ion exchanged, given 4 contacts at room temperature with a 5 weight percent  $\text{NH}_4\text{Cl}$  solution using 20 pounds of solution per pound of zeolite. The crystalline aluminosilicates were washed free of chloride, dried and then recalcined for 10 hours at 1000°F. in air.

Both samples of ZSM-5 were then evaluated for catalytic activity employing n-hexane cracking in the "alpha" test. The "alpha" test is described by P. B. Weisz and J. N. Miale in "Journal of Catalysis", Volume 4, No. 4, August 1965, pages 527–9. The results of this evaluation, shown in the following table, again demonstrate the improved catalytic activity resulting when silica occlusion is reduced by the incorporation of an added salt to the zeolite synthesis reaction mixture.

Effect of "Salting" on HZSM-5 Catalytic Activity		
NaCl in reaction mixture	0	16.7 pounds
n-hexane $\alpha$ at 800°F.	480	620

## EXAMPLE 4

In order to illustrate that the enhancement of catalytic activity due to the reduction of silica occlusion is most effective with crystalline aluminosilicates having a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio greater than 6, two samples of faujasite were prepared by identical techniques differing only in that NaCl was added to the reaction mixture of one sample.

The basic method of formulation was that 30 grams of Georgia Kaolin, calcined 6 hours at 1700°F., was blended with 150 grams of Georgia Kaolin calcined 6 hours at 1500°F. This dry mixture was slowly added to a solution containing 75 grams of NaOH (98.2 percent NaOH), 361 grams of Q-brand sodium silicate and 69 grams of 50 weight percent solution of tetramethylammonium chloride in water while being agitated on a Waring Blender. After the clay had been added, the mixing was continued for 30 seconds. The mixture was transferred to a polypropylene jar and put into a steam chest at 100°C. to crystallize. After 115 hours the sample was removed, a portion was washed free of the mother liquor and dried. X-ray diffraction analysis of the dried product determined the product to be synthetic faujasite.

An identical preparation was made differing only in that 60 grams of NaCl were added to the zeolite synthesis reaction mixture. The crystallized product of this preparation was also identified as faujasite.

Both samples were washed free of excess alkali and soluble silicates and dried at 120°C. The dried samples were then given four 1 hour rare earth ion exchanges at 180 to 200°F. using 400 grams of 8 percent  $\text{RECl}_3 \cdot 6\text{H}_2\text{O}$  solution per 100 grams of dried zeolite. The samples were then washed chloride free, dried at 120°C. and calcined 3 hours at 1000°F. in dry air.

Both catalysts were then evaluated for catalytic activity employing the same n-hexane "alpha" test. The results of this test along with the comparison of the catalytic activities of higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio crystalline aluminosilicates, with and without salt addition to the zeolite synthesis reaction mixture, are presented in the following table. The results clearly demonstrate that the reduction of silica occlusion is much more effective in increasing catalytic activity of the higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio ( $>6$ ) zeolites than with lower  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio zeolites such as faujasite.

Effect of "Salting" on various  $\text{SiO}_2/\text{Al}_2\text{O}_3$  Ratio Zeolites

	Crystalline Aluminosilicates	$\text{SiO}_2/\text{Al}_2\text{O}_3$	Salted	$\alpha$ at 800°F.	Catalytic Activity LTD $k_1$ // mole-sec. $\times 10^6$	
40	ZSM-4	6.7	No		2.4	40
			Yes		82	
	ZSM-5	$>50$	No	480		
			Yes	620		
45	Faujasite	4.5 to 5.0	No	200		45
			Yes	100		

The slight difference in "alpha" for faujasite can be accounted for by the fact that the salted preparation had a slightly higher sodium content after rare earth exchange which would tend to lower its catalytic activity.

## EXAMPLE 5

In order to illustrate the actual filtration and washing improvements of a zeolite designated ZSM-4 and described hereinbelow, two samples of this ZSM-4 were synthesized, one batch containing 7.5 weight percent, based on the reaction mixture, of added sodium chloride in the reaction gel before the crystallization. A filter leaf study was conducted on the synthesized form of the sodium ZSM-4 which existed as a slurry in its mother liquor. The slurry concentrations varied between 8.3 and 8.6 percent by weight after adjusting with water. The equipment and procedure for conducting the filter leaf tests are in accordance with that presented in the "Chemical Engineer's Handbook", Fourth Edition edited by Perry, Chilton and Kirkpatrick, pgs. 19-59. A filter leaf having an area of 0.1 square foot in size was employed. The filter leaf was a nylon cloth. In all experiments reported below, eighteen inches of vacuum was applied

with a 40 seconds submergence for cake deposition and then 80 seconds for the dewatering in the atmosphere. The weight of filtrate and solids collected are shown in Table 1. The higher numbers for the runs wherein the sodium chloride was employed in the reaction mixture indicate that a greater amount of slurry was filtered. This is due to the better filterability of the material due to the flocculating effect of the salt on the dispersed crystalline aluminosilicate. Thus, the filter media, i.e. the nylon cloth and the deposited ZSM-4 zeolite is substantially more porous than those samples wherein no added salt was employed during crystallization and formation of the zeolite. The results reported below show that the slurries that contain chloride have a much higher rate of filtration, especially at higher temperatures around, for instance, 160°F. At the outlet, it should be noted that the physical properties of the filter cakes collected also show great differences. Those preparations wherein no sodium chloride was added resulted in a filter cake thus described as thixotropic as usual, i.e. they were generally a dense phase. The preparations employing sodium chloride resulted in a firm, but porous, mass which was easy to handle in subsequent operations. The substantially lower water content of the filter cake resulting from the preparation employing the "salting" technique of the present invention is also advantageous.

TABLE 1  
Filter Leaf Studies on ZSM-4 Filtration

	NaCl Temp (°F.)			7.5% wt	
		room	152	room	152
	Time of Filtration				
	In Slurry (Sec)	40	40	40	40
	Dry (Sec)	80	80	80	80
	Filtrate (1) (gm)	141.6	235.5	292.2	666.6
	Wet Cake (1) (gm)	64.2	99.2	67.1	135.9
	Solids in Cake (gm)	30.5	48.9	37.1	80.7
	Thickness of Cake	1/8"	3/16"	3/16"	7/16"
	Solids Content of				
	Cake, % wt	47.5	49.3	55.4	59.5
	Note	Thixotropic Cake		Firm and Porous	

(1) Average value of triplicate determinations.

#### Liquid Toluene Disproportionation Test

The liquid toluene disproportionation test (LTD) used herein has been developed using a microreactor (less than 20 cc. of catalyst) and full size catalyst particles that give kinetically consistent data. The range of catalyst volumes and liquid flow rates employed are above the range where axial diffusion effects might be significant and below the range where bypassing, short circuiting or excessive backmixing could give erroneous results.

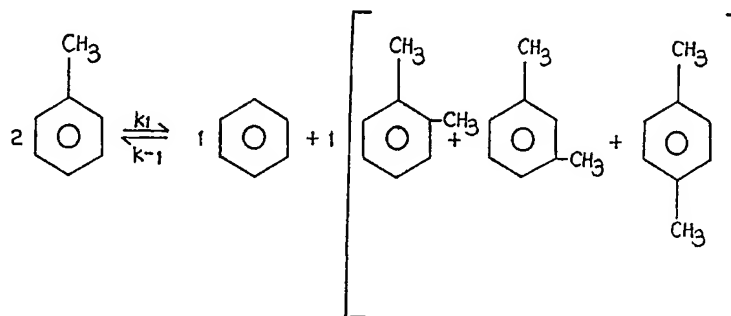
The apparent activation energy for liquid phase toluene disproportionation has been found to be 24 kcal/g. mole. The ageing rate, i.e. the rate of decline of the second order reaction rate constant with time on stream, was found to be a first order decay with two distinct ageing rates over a 24-hour period.

#### LTD Experimental Procedure

The experimental evaluations were conducted using a microreactor (15 cc. max. volume), reagent grade toluene (percolated through alumina). The operating procedure was to fill the complete reaction system with liquid at room temperature then raise the temperature to the operating temperature in 40 minutes or less. When the catalyst bed reached reaction temperature, this was taken as the reference to zero time. The product was continually collected over the course of the run, but only that product collected over the final five minutes of the time period specified was used for product analysis. That is to say that the product analysis reported for a sample after one hour on stream was for a sample taken for the time period 55—60 minutes.

The product analysis was performed by gas phase chromatography employing an F&M Model 5754 temperature programmed for 80 to 125°C. at 4°C./min. and using helium as a carrier gas at 50 cc./min. A 24-foot chromatographic column was employed packed with 4 percent diisodecaphthalate, 4 percent bentone 34 supported on 60 to 80 mesh Chromosorb W HMDS.

LTD Results and Discussion  
The kinetic model used was for the reaction:



5 which is a second order reaction in toluene and assumes that all three xylenes behave as a single species. The integrated rate equation is readily derived or can be found in several reference texts. Employing the same equilibrium values for reactant and products reported, the following expression for the reaction rate constant,  $k_1$ , was obtained: 5

$$k_1 = \frac{1}{t} (0.073 \ln 0.16 \left( \frac{3.62 - X}{0.58 - X} \right))$$

10 where

$t$ —residence time, sec.

$X$ —toluene conversion, weight percent

The process of the present invention is particularly suitable in preparing composite catalysts comprising alumina and relatively new zeolites known as ZSM-4. ZSM-4 compositions can also be identified, in terms of mole ratios of oxides, as follows:

$$15 \quad 0.9 \pm 0.2 \frac{M_2O}{n} : Q_2O_3 : 6-20 RO_2 : zH_2O \quad 15$$

wherein  $M$  is a cation,  $n$  is the valence of said cation,  $Q$  is aluminum,  $R$  is silicon, and  $z$  is from 0 to 20. In a preferred form, the zeolite has a formula, in terms of mole ratios of oxides, as follows:

$$0.9 \pm 0.2 \frac{M_2O}{n} : Al_2O_3 : 6-20 SiO_2 : zH_2O$$

20 and  $M$  is selected from the group consisting of a mixture of tetramethylammonium cations and alkali metal cations, especially sodium. The original cations can be at present so that the amount of tetramethylammonium cations is between 1 and 50 percent of the total amount of the original cations. Thus, the zeolites can be expressed by the following formula, in terms of mole ratios of oxides:

$$25 \quad 0.9 \pm 0.2 [xR'_2O + (1-x) \frac{M_2O}{n}] : Q_2O_3 : 6-20 RO_2 : 0-20 H_2O \quad 25$$

wherein  $Q$  and  $R$  have the previously assigned significance,  $R'$  is tetramethylammonium,  $M$  is an alkali metal cation and  $x$  is between 0.01 and 0.50.

Members of the family of ZSM-4 zeolites possesses a definite distinguishing crystal-line structure whose X-ray diffraction pattern has the following values:

TABLE 1—A

	Interplanar Spacing d(Å)	Relative Intensity	
	9.1 ± .2	vs	
	7.94 ± .1	mw	
5	6.90 ± .1	m	5
	5.97 ± .07	s	
	5.50 ± .05	mw	
	5.27 ± .05	mw	
	4.71 ± .05	mw	
10	4.39 ± .05	w	10
	3.96 ± .05	w	
	3.80 ± .05	s	
	3.71 ± .05	m	
	3.63 ± .05	m	
15	3.52 ± .05	s	15
	3.44 ± .05	m	
	3.16 ± .05	s	
	3.09 ± .05	m	
	3.04 ± .05	m	
20	2.98 ± .05	m	20
	2.92 ± .05	s	

These values were determined by standard techniques. The radiation was the K-alpha doublet of copper, and a Geiger counter spectrometer with a strip chart pen recorder was used. The peak heights,  $I$ , and the positions as a function of 2 times theta, where theta is the Bragg angle, were read from the spectrometer chart. From these, the relative intensities,  $100 I/I_0$ , where  $I_0$  is the intensity of the strongest line or peak, and  $d$  (obs.), the interplanar spacing in Å., corresponding to the recorded lines, were calculated. In Table 1—A, the relative intensities are given in terms of the symbols s=strong, m=medium, mw=medium weak, vs=very strong, and w=weak.

Zeolite ZSM-4 can be suitably prepared by preparing a solution containing  $R'_2O$  (where  $R'$  is a tetramethylammonium cation), sodium oxide, an oxide of aluminum, an oxide of silica, and water and having a composition, in terms of mole ratios of oxides, falling within the following ranges:

TABLE 2

	Broad	Preferred	
35			35
	$Na_2O/(R'_2O + Na_2O)$	.31 to <1	.75 to .99
	$(R'_2O + Na_2O)/RO_2$	.05 to .90	.15 to .75
	$RO_2/Q_2O_3$	3 to 60	6 to 30
	$H_2O/(R'_2O + Na_2O)$	15 to 600	20 to 150

wherein  $R'$  is a tetramethylammonium cation, Q is aluminum and R is silicon, maintaining the mixture until crystals of the zeolite are formed. Thereafter, the crystals are separated from the liquid and recovered, as an aluminosilicate.

The process of the present invention is also particularly suitable in preparing relatively new zeolites known as ZSM-5. ZSM-5 compositions can also be identified, in terms of mole ratios of oxides, as follows:

$$0.9 \pm 0.2 \frac{M_2O}{n} : Q_2O_3 : 6-100 RO_2 : zH_2O$$

wherein M is a cation, n is the valence of said cation, Q is aluminum, R is silicon and z is from 0 to 40. In a preferred synthesized form, the zeolite has a formula, in terms of mole ratios of oxides, as follows:

$$0.9 \pm 0.2 \frac{M_2O}{n} : Al_2O_3 : 6-100 SiO_2 : zH_2O$$

and M is selected from the group consisting of a mixture of alkali metal cations, especially sodium, and tetraalkylammonium cations, the alkyl groups of which preferably contain 2—5 carbon atoms.

Members of the family of ZSM-5 zeolites possess a definite distinguishing crystal-line structure whose X-ray diffraction pattern shows the following significant lines:

TABLE 3

	Interplanar Spacing d(A)	Relative Intensity		
5	11.1 ± 0.3	s	5	
	10.0 ± 0.3	s		
	7.4 ± 0.2	w		
	7.1 ± 0.2	w		
	6.3 ± 0.2	w		
10	6.04 ± 0.2	w	10	
	5.97 ± 0.2	w		
	5.69 ± 0.1	w		
	5.56 ± 0.1	w		
	5.01 ± 0.1	w		
15	4.60 ± 0.1	w	15	
	4.35 ± 0.1	w		
	4.25 ± 0.1	w		
	3.85 ± 0.1	vs		
	3.75 ± 0.05	s		
20	3.71 ± 0.05	s	20	
	3.64 ± 0.05	m		
	3.04 ± 0.05	w		
	2.99 ± 0.05	w		
	2.94 ± 0.05	w		
25	These values were determined by standard techniques. The radiation was the K-alpha doublet of copper, and a scintillation counter spectrometer with a strip chart pen recorder was used. The peak heights, I, and the positions as a function of 2 times theta, where theta is the Bragg angle, were read from the spectrometer chart. From these, the relative intensities, 100 I/I., where I. is the intensity of the strongest line or peak, and d (obs.), the interplanar spacing in A, corresponding to the recorded lines, were calculated. In Table 3, the relative intensities are given in terms of the symbols s=strong, m=medium, w=weak, and vs=very strong.			25
30	Zeolite ZSM-5 can be suitably prepared by preparing a solution containing tetra-propyl ammonium hydroxide, sodium oxide, an oxide of aluminum, an oxide of silica, and water and having a composition falling within the following ranges:			30
35				35

TABLE 4

		Broad	Preferred	Particularly Preferred	
40	OH <sup>-</sup> /RO <sub>2</sub>	0.07—10.0	0.1—0.8	0.2—0.75	
	R' <sub>4</sub> N <sup>+</sup> (R' <sub>4</sub> N <sup>+</sup> + Na <sup>+</sup> )	0.2—0.95	0.3—0.9	0.4—0.9	40
	H <sub>2</sub> O/OH <sup>-</sup>	10—300	10—300	10—300	
	RO <sub>2</sub> /Q <sub>2</sub> O <sub>3</sub>	5—100	10—60	10—40	

wherein R' is propyl, Q is aluminum and R is silicon and OH<sup>-</sup> refers to hydroxyl ion present by virtue of substances additional to water per se, maintaining the mixture until crystals of the zeolite are formed. It is noted that an excess of tetrapropylammonium hydroxide can be used which would raise the value of OH<sup>-</sup>/RO<sub>2</sub> above the ranges set forth supra. The excess hydroxide, of course, does not participate in the reaction. Thereafter, the crystals are separated from the liquid and recovered. Typical reaction conditions consist of heating the foregoing reaction mixture to a temperature of from about 100°C. to 175°C. for a period of time of from about six hours to 60 days. A more preferred temperature range is from about 150 to 175°C. with the amount of time at a temperature in such range being from about 12 hours to 8 days.

#### WHAT WE CLAIM IS:—

1. A method of synthesizing a crystalline aluminosilicate zeolite having a silica: alumina mole ratio greater than 6, which method comprises forming a reaction mixture containing silica, alumina, cations and water in the proportions required for crystallization therefrom of a crystalline aluminosilicate zeolite of a predetermined composition, said reaction mixture further containing an amount surplus to said required pro-



portions and having no influence upon said predetermined composition, of a solution of, an alkali metal salt (as herein defined), and recovering from said mixture a crystalline aluminosilicate zeolite substantially free of pore obstruction by silica and having said predetermined composition.

- 5 2. A method according to Claim 1, wherein the normality of the salt solution is less than 1. 5
3. A method according to any preceding Claim, wherein said salt is a sodium salt.
4. A method according to Claim 3, wherein said salt is sodium chloride.
5. A method according to Claim 3, wherein said salt is sodium sulfate.
- 10 6. A method according to Claim 1 or 2, wherein said reaction mixture is a precursor of zeolite ZSM-4 and comprises the following substances expressed as oxides in the mole ratios set forth: 10

15	$\text{Na}_2\text{O}/(\text{R}'_2\text{O} + \text{Na}_2\text{O})$	0.31 to <1	15
	$(\text{R}'_2\text{O} + \text{Na}_2\text{O})/\text{RO}_2$	0.05 to 0.90	
	$\text{RO}_2/\text{Q}_2\text{O}_3$	3 to 60	
	$\text{H}_2\text{O}/(\text{R}'_2\text{O} + \text{Na}_2\text{O})$	15 to 600	

wherein R' is a tetramethylanmonium cation, Q is aluminium and R is silicon.

7. A method according to Claim 6 wherein said ratios are as follows:

20	$\text{Na}_2\text{O}/(\text{R}'_2\text{O} + \text{Na}_2\text{O})$	0.75 to 0.99	20
	$(\text{N}'_2\text{O} + \text{Na}_2\text{O})/\text{RO}_2$	0.15 to 0.75	
	$\text{RO}_2/\text{Q}_2\text{O}_3$	6 to 30	
	$\text{H}_2\text{O}/(\text{R}'_2\text{O} + \text{Na}_2\text{O})$	20 to 150	

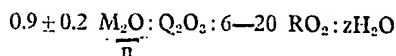
8. A method according to Claim 1 or 2 wherein said reaction mixture is a precursor of zeolite ZSM-5 and comprises the following components in the mole ratios set forth: 25

$\text{OH}^-/\text{RO}_2$	0.07—10.0
$\text{R}'_4\text{N}^+ / (\text{R}'_4\text{N}^+ + \text{Na}^+)$	0.2—0.95
$\text{H}_2\text{O}/\text{OH}^-$	10—300
$\text{RO}_2/\text{Q}_2\text{O}_3$	5—100

- wherein R' is a propyl, Q is aluminium and R is silicon. 30
9. A method according to Claim 8 wherein said mole ratios are as follows:

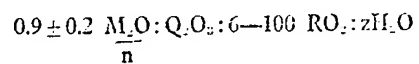
35	$\text{OH}^-/\text{RO}_2$	0.1—0.8	35
	$\text{R}'_4\text{N}^+ / (\text{R}'_4\text{N}^+ + \text{Na}^+)$	0.3—0.9	
	$\text{H}_2\text{O}/\text{OH}^-$	10—300	
	$\text{RO}_2/\text{Q}_2\text{O}_3$	10—60	

10. A method according to any of Claims 1 to 5 wherein said crystalline zeolite has an X-ray diffraction pattern of Table 1—A of the specification, and a composition expressed in terms of mole ratios of oxides, as follows:



- where M is a cation, n is the valence of said cation, Q is aluminium, R is silicon and z is from 0 to 20. 40

11. A method according to any of Claims 1 to 5 wherein said crystalline zeolite has an X-ray diffraction pattern of Table 3 of the specification, and a composition, expressed in terms of mole ratios of oxides, as follows:



wherein M is at least one cation, n is the valence of said cation, Q is aluminium, R is silicon and z is from 0 to 40.

12. A method according to claim 1 substantially as hereinbefore described.

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